

IV. *On the Discharge of Negative Electricity from Hot Calcium and from Lime.*

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INTRODUCTION.

THE discharge of electricity from hot metals has been the subject of a great number of researches by different authors. The metal chiefly used in these experiments has been platinum, on account of its high melting-point, its stability in air, and the ease with which it can be obtained in a state of purity. In the present experiments calcium was chosen for investigation because of its strong electropositive character. Since this implies a great attraction for positive electricity, it would be expected that the negative corpuscles would escape more readily from calcium than from platinum. It should, therefore, be possible to obtain a measurable "negative leak" from calcium at a much lower temperature than from platinum or other less electropositive metal.

The first method of experimenting employed consisted in measuring the saturation current from an electrically heated calcium wire to a surrounding electrode, both being placed in a vacuum, but it was found to be impossible to get a clean surface of calcium in this way, for the metal combines with the oxygen, nitrogen, and water vapour in the air, and becomes more or less covered with a coating of calcium compounds before the apparatus can be fitted up. Another difficulty was soon discovered. When the wire was heated to above a dull red heat, the vapour pressure of the metal was sufficient for it to volatilize and condense on the colder walls of the tube. Thus the wire got thinner at its hottest point, and, consequently, the temperature there rose, and the sublimation increased, until in a few seconds the wire had broken through.

It was finally decided to make use of the volatility of calcium in order to obtain a clean surface of the metal. The method of experiment was to fix up a platinum strip as the cathode in a vacuum tube and to ascertain the manner in which the current from this to the other electrode varied with the temperature of the strip, with the difference of potential between the electrodes, and with the gas pressure in the

apparatus. The platinum strip was then covered with a layer of calcium by means of sublimation, and the current between the two electrodes was measured again. It might here be stated that a current between the two electrodes was observed only when the platinum strip was used as the cathode, the positive leak being too small to be detected by the galvanometer used. In what follows, therefore, the platinum strip will be spoken of as the cathode.

When the observations of the negative leak from the calcium-covered cathode had been made, the calcium was oxidised to lime, and the leak measured again. In this way the negative leak from metallic calcium was compared with the negative leak from the same amount of metal in the form of oxide. The full account of the experiments and results is divided for convenience into the following sections:—

- (1) Description of the apparatus, &c. ;
- (2) Investigation of the negative leak from platinum ;
- (3) The negative leak from calcium in helium ;
- (4) The negative leak from lime in helium and in hydrogen ;
- (5) Summary of results, and conclusion.

(1) *Description of the Apparatus, &c.*

The glass apparatus shown in fig. 1 was found to be the most convenient form of discharge tube for these experiments.

A is a platinum strip which can be heated electrically, the current being supplied by means of the thick platinum leads G. The leak from this to the platinum electrodes B, C, which together form the anode, was measured by means of a delicate d'Arsonval galvanometer, giving a deflection of 1 millim. for a current of 7.19×10^{-10} ampère. The calcium wire D, from which the metal is to be sublimed, is beneath the platinum strip, and about two centimetres from it. It can be heated by an electric current led in through the thick copper leads F, which enter the bulb through sealing-wax joints. The apparatus is connected with the mercury pump McLeod gauge and P_2O_5 drying bulb by the side tube shown in the figure. The platinum strip was 3.5 centims. long and 2 millims. wide. The calcium wire was about 6 centims. long and 1 millim. in diameter.

Since calcium is readily attacked by all the more common gases, the experiments had to be conducted in an atmosphere of argon or helium. Either of these gases could be admitted into the apparatus through a side tube. For the purpose of purifying the gas a small discharge tube was fitted on to the apparatus. In this the cathode was an alloy of potassium and sodium, made by mixing the metals in atomic proportions. When a discharge from an induction coil is sent through this tube the alloy gradually absorbs any gas that may be present, except argon or helium. The argon or helium in the apparatus could thus be purified by running the discharge

tube until the pressure as indicated on the MacLeod gauge remained constant. In the first experiments the gas employed was argon, while in the later experiments helium gas was used. The helium was purchased out of a grant obtained from the Royal Society.

The arrangement of apparatus used to measure the current from the surface of the platinum is indicated in fig. 2.

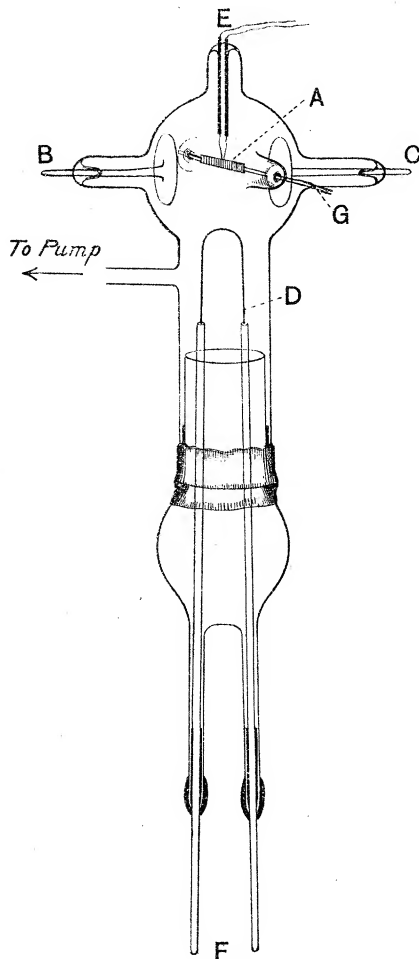


Fig. 1.

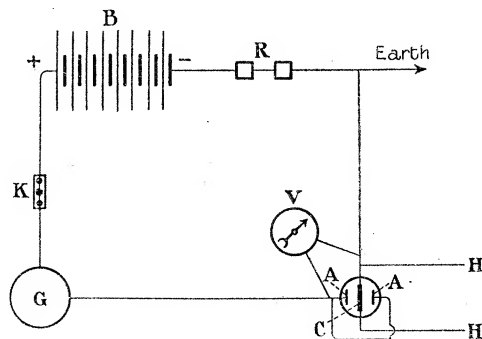


Fig. 2.

A, A, platinum anodes; C, platinum strip; H, H, leads of heating circuit; V, voltmeter; B, battery; K, key; G, galvanometer; R, tin-foil fuse.

One end of the platinum strip C was connected to earth and also, through a fine tin-foil fuse, R, to the negative pole of a battery of small storage cells, B. The positive pole of this battery was connected to the anodes A, through the key K, and the sensitive d'Arsonval galvanometer G, which was well insulated on paraffin blocks and served to measure the current. The difference of potential between the electrodes A and C was determined by means of the electrostatic voltmeter V. H, H, are the leads for heating the platinum strip.

The temperature of the cathode was determined by means of a thermocouple which was welded on to the strip at its middle. The wires forming the thermocouple were

pure platinum, and platinum with 10 per cent. of rhodium. They were of very small diameter (0.0025 centimetre), so that the temperature of the strip was not materially lowered by the heat conducted along them. Each wire was sealed into a fine glass tube, and these tubes were sealed into the bulb vertically above the platinum strip at E (fig. 1). The other ends of the thermocouple wires were some 20 centims. away and were soldered on to wires from a d'Arsonval galvanometer, the junctions being enclosed in a water jacket, through which a stream of water, at a known constant temperature, was kept circulating. The thermocouple was standardised before the platinum strip was placed in the bulb. Very small grains of pure potassium sulphate were placed on the strip near to the junction. The strip was then heated by an electric current, which was increased until the grains of sulphate (observed through a microscope) just melted. The galvanometer deflection corresponding to this temperature was noted. Use was then made of the curve given by CALLENDAR* for transposing the galvanometer readings into degrees Centigrade.

(2) *Investigation of the Negative Leak from Platinum.*

Professor H. A. WILSON has shown that, in order to get constant values of the negative leak from platinum, great care must be taken to remove all traces of hydrogen, as this gas has a huge effect on the negative leak. For this purpose Professor WILSON recommends boiling the platinum in nitric acid. This method was adopted in the present research. The apparatus shown in fig. 1 consists of two parts, the lower of which, holding the calcium wire and leads, slides into the upper part and is held in position by a sealing-wax joint. When the apparatus had been made, the upper part containing the platinum strip to be used as a cathode was inverted and filled with strong nitric acid. This was boiled for about an hour, and then the acid was replaced by a fresh supply, which was also boiled for some time. After several boilings with strong nitric acid the apparatus was washed out with distilled water and dried by sucking dry air, filtered by passing through cotton wool, through it by means of a water pump. The calcium wire was carefully cleaned with fine emery paper and quickly sealed in position. The whole apparatus was then fixed on to the mercury pump, and the air pumped out until a good vacuum was obtained. The platinum strip was raised to incandescence by means of the current from 10 E.P.S. motor cells. After the platinum strip had been treated with nitric acid there was found to be only a slight increase of gas pressure inside the apparatus when the strip was left at a high temperature for a long time. The slight evolution of gas is probably hydrogen, which had been occluded in the platinum and was not completely eliminated by boiling with nitric acid. The negative leak from the platinum was found to decrease slightly as the gas was evolved, but it soon became fairly constant.

* CALLENDAR, 'Phil. Mag.,' vol. 48, p. 519.

In some cases the attainment of the constant state was hastened by repeatedly washing the apparatus out with dry air and heating the platinum in that gas. When the pressure did not increase on heating the platinum, the apparatus was pumped down to as low a pressure as possible, and helium was let in to a pressure of 3 or 4 millims. The sodium-potassium alloy was then let into the special discharge tube through a well fitting tap, and the helium purified in the manner already described.

The relation between the current and the electromotive force was first investigated. The results obtained were similar to those found by other observers for the negative leak in air, oxygen, or nitrogen. For instance, at a pressure of 0.005 millim. the current was saturated with a potential difference of 30 volts, the distance between the electrodes being about 2 centims. With higher pressures of gas in the apparatus the potential difference required to saturate the current was much greater, on account of the formation of new ions by collisions with the gas molecules. With pressures above about 0.01 millim. the current never became saturated, but increased more and more rapidly with the potential as the latter was raised.

Mention must be made of a curious increase in the negative leak which was obtained whenever the cathode was allowed to remain for some time in a good vacuum. For instance, if the apparatus was left at a low pressure (0.005 millim.) over night, the leak was always found to be much larger when tested on the following day. This increase was sometimes as much as a thousand times the normal current. It gradually died away when the cathode was left at a bright red heat for some time. On investigating this effect it was found that the increased leak was connected with the appearance of a dark substance on the surface of the platinum strip. The amount of this was very small, and it was only visible when the platinum was heated. It disappeared on long continued heating, and its disappearance was always accompanied by a huge decrease in the negative leak. This phenomenon only occurred at low pressures. When the apparatus was left at a pressure of 2 or 3 millims., the negative leak was found to remain practically constant. An effect similar to this seems to have been obtained by Professor H. A. WILSON in his experiments on the discharge of electricity from hot platinum. He says*: "If the wire is simply left standing in air at a low pressure for a long time, the leak is often greater than before on again heating the wire." I think that the black stuff which could be seen on the platinum strip in my apparatus must have been some compound formed by the action of the mercury vapour upon the platinum. WILSON found that mercury vapour increases the negative leak very considerably at high temperatures. This seems to indicate that there is some action between the two metals.

The leak would sometimes increase enormously when the apparatus was left at a low pressure for only a few minutes; sometimes even in the course of an observation it would increase to ten or twenty times the normal value. In one case a platinum

* H. A. WILSON, 'Phil. Trans.' A, vol. 202, p. 243, 1903.

strip gave a leak of 3.76×10^{-9} ampère with a potential difference of 40 volts at a temperature of 1480°C . and pressure 0.0042 millim. of mercury. On testing again, two hours later, at the same temperature and pressure, the leak was 5.05×10^{-6} ampère!

This increase of the negative leak on standing at low pressures rendered it necessary to have a pressure of several millimetres when comparing the negative leak before and after subliming the calcium on to the cathode. Some observations were therefore made to ascertain the manner in which the leak from the hot platinum varies with the gas pressure in the apparatus over the range of pressures likely to be used in the subsequent experiments. It was found that with 40 volts difference of potential between the electrodes the negative leak at a constant temperature was nearly independent of the gas pressure between 7.5 millims. and 3 millims. If the pressure was reduced below this, the leak decreased gradually until a very low pressure was reached, when it suddenly increased again to many times its former value. This increase is probably due to the cause mentioned above. It did not always occur at exactly the same pressure, but generally at pressures below 0.1 millim. Sometimes it only appeared after allowing the apparatus to remain at a low pressure for several hours.

The conclusion from these experiments is that, for the purpose of comparing the negative leak from platinum with that from calcium or lime, it is best to work with a gas pressure of a few millimetres of mercury and to use a constant voltage of 40 volts, for the current never becomes saturated at this pressure. Working with a constant voltage comes to practically the same thing as measuring the saturation current in each case, for the current passing under a constant electromotive force should be proportional to the number of ions liberated at the surface of the cathode.

The following table contains the values of the negative leak from the platinum strip at different temperatures in helium at a pressure of 3.236 millims. with a potential difference of 40 volts between the electrodes. The series of observations was repeated several times during the course of two or three days, and the values given were found to be practically constant. The numbers in brackets refer to the order in which the measurements were made.

TABLE I.—Negative Leak from Platinum in Helium Gas at a Pressure of 3.236 millims.

	Temperature, $^{\circ}\text{C}$.	Negative leak per square centimetre (ampère).
(1)	1331	1.95×10^{-9}
(2)	1468	3.96×10^{-8}
(3)	1542	1.75×10^{-7}
(4)	1571	2.99×10^{-7}
(5)	1610	5.91×10^{-7}

The values given above are slightly smaller than those given by H. A. WILSON for the negative leak per square centimetre from platinum in air at a low pressure.

Professor WILSON gives for the leak at 1545°C. the value 6.38×10^{-7} ampère. The smallest value I ever obtained for the negative leak in helium was 6.91×10^{-8} ampère per square centimetre of platinum surface at 1540°C. By taking great precautions in cleaning his platinum wires and purifying the air in the apparatus, with a special view to getting rid of all traces of hydrogen evolved by the wire when heated, Professor WILSON was able to reduce the leak to 10^{-8} ampère per square centimetre of surface at 1616°C. The values given in Table I. for the negative leaks in helium at different temperatures could be reduced to about one-tenth by reducing the pressure of the gas in the apparatus. Since Professor WILSON's results were obtained in a good vacuum, it seems that the value of the negative leak in helium is practically the same as in air under similar conditions of temperature and pressure.

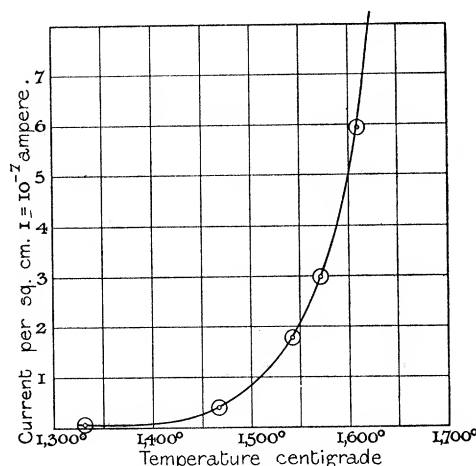


Fig. 3. Relation between negative leak and temperature of platinum cathode in helium gas at 3.236 millims. pressure.

From the numbers in Table I. the curve in fig. 3 was drawn. It is similar to the current-temperature curves obtained by other observers in air.

O. W. RICHARDSON and H. A. WILSON have found that the variation of the negative leak with temperature can be expressed by an equation of the type

$$x = A\theta^k e^{-Q/2\theta},$$

where x is the current in ampères, θ the absolute temperature, and Q and A are constants. Q is a measure of the work done by a corpuscle in escaping from the surface of the metal; it can be obtained from any two values of x by means of the equation

$$Q = 2 \frac{\log_e x_2/x_1 - \frac{1}{2} \log_e \theta_2/\theta_1}{\theta_1^{-1} - \theta_2^{-1}}.$$

By the use of this formula the following values of Q were obtained from the observed currents. The numbers in brackets refer to the observations in Table I., which were used in calculating the value of Q .

TABLE II.—Values of the Constant Q calculated from Observations of Table I.

From observations	Mean temperature, °C.	Q (calories).
(1, 2)	1400	121,100
(2, 3)	1505	125,100
(3, 4)	1557	121,800
(4, 5)	1591	119,500
		Mean = 121,900.

The variations in Q are not greater than can be accounted for by the errors of experiment. The mean value is lower than that given by WILSON (viz., 131,100), but this is probably due to the fact that the present experiments were performed with a gas pressure of several millimetres in the apparatus, whereas WILSON's result was obtained in a good vacuum.

Taking $Q = 121,900$ and the current per square centimetre at 1610°C. as 5.91×10^{-7} ampère, the value of the constant A in the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$ is 1.55×10^6 , so that the equation for the current x (ampères) at the absolute temperature θ becomes

$$x = 1.55 \times 10^6 \theta^{\frac{1}{2}} e^{-121,900/2\theta}.$$

The following is a comparison of the currents calculated by means of this equation and those found experimentally.

TABLE III.

Temperature, °C.	Negative leak in ampères per square centimetre.	
	Observed.	Calculated.
1331	1.95×10^{-9}	1.96×10^{-9}
1468	3.96×10^{-8}	4.06×10^{-8}
1542	1.75×10^{-7}	1.73×10^{-7}
1571	2.99×10^{-7}	2.95×10^{-7}
1610	5.91×10^{-7}	5.91×10^{-7}

The observed and calculated values of the current agree very well, showing that the formula expresses the experimental results with considerable accuracy.

(3) *The Negative Leak from Calcium in Helium.*

Having shown that the negative leak from the platinum strip was of the normal amount, and that it varied with the temperature according to the established law, calcium was sublimed on to it and the alteration of the leak caused thereby was investigated. The sublimation of the calcium was performed by connecting the thick copper leads of the calcium wire (F, fig. 1) to the alternating current from a transformer and gradually decreasing the resistance in the circuit until the calcium became red hot. It then sublimed, and the bulb was covered with a fine metallic mirror, and the electrodes would be similarly covered with calcium. With practice it was possible to regulate the current so that the wire did not fuse through on the first heating. After observations of the negative leak had been taken, more calcium could be sublimed on to the cathode, and the observations repeated. The gas pressure in the apparatus increased during the process on account of the gas evolved by the calcium. The discharge was therefore started in the potassium-sodium tube and kept going until the whole of the evolved gases were absorbed by the alloy and the apparatus contained only helium gas at the same pressure as before. In order to see if the evolved gas increased the leak from the platinum strip, an experiment was

made in which the calcium wire was warmed sufficiently to expel some gas from it, but not to a high enough temperature to cause it to volatilize on to the platinum. The evolved gas was then absorbed in the potassium-sodium alloy, and the leak from the platinum strip in helium gas was again tested. It was found to be the same as before the calcium wire had been heated.

The negative leak from the calcium-covered strip was found at several temperatures. The observed values are given in the following table. The potential difference between the electrodes was 40 volts, and the gas pressure, as before, 3.236 millims.

TABLE IV.

Temperature.	Current in ampères per square centimetre.		Q (calories).
	Observed.	Calculated.	
° C.			
840	3.92×10^{-9}	3.44×10^{-9}	4.32×10^{-4}
919	1.47×10^{-8}	3.11×10^{-8}	9.01×10^{-4}
986	1.13×10^{-7}	1.63×10^{-7}	5.01×10^{-4}
1005	1.53×10^{-7}	2.52×10^{-7}	7.67×10^{-4}
1050	4.32×10^{-7}	6.75×10^{-7}	9.33×10^{-4}
1065	6.45×10^{-7}	9.27×10^{-7}	9.11×10^{-4}
1117	2.35×10^{-6}	2.61×10^{-6}	9.62×10^{-4}
1142	4.37×10^{-6}	4.19×10^{-6}	8.99×10^{-4}
1220	2.36×10^{-5}	1.66×10^{-5}	5.44×10^{-4}
1238	2.95×10^{-5}	2.23×10^{-5}	7.42×10^{-4}
1310	9.22×10^{-5}	1.47×10^{-4}	4.32×10^{-4}
1385	1.75×10^{-4}	1.98×10^{-4}	

Mean value of Q = 7.29×10^{-4} .

The observed currents in the table are plotted against the corresponding temperatures in fig. 4. The unit of current is successively multiplied by ten in passing to the right from one curve to the next.

It will be seen that the curves obtained are exactly similar to those given by platinum.*

The observations of the negative leak from calcium were made as quickly as

* See RICHARDSON, 'Phil. Trans.,' A, vol. 201, p. 497.

possible, because the calcium gradually sublimed off the platinum strip if left heating for a long time. It is somewhat surprising that it remained on long enough for the above readings to be taken. The explanation is, probably, that the calcium melts

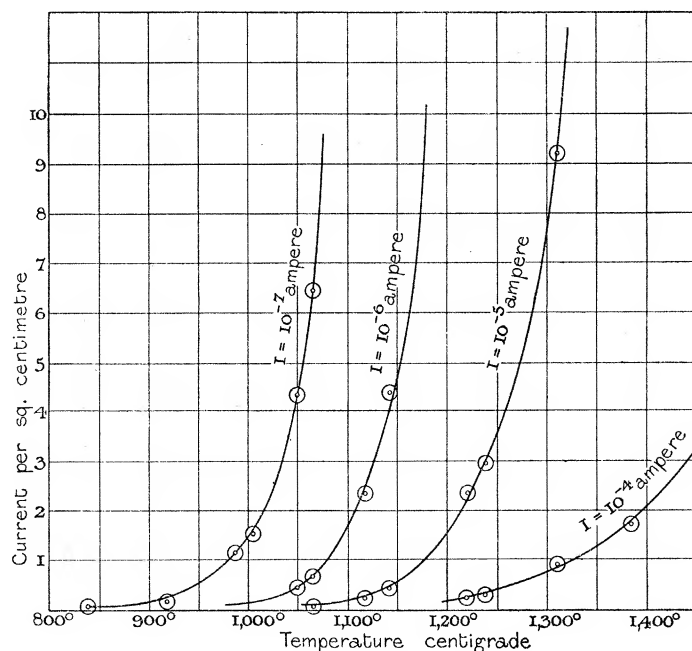


Fig. 4. Relation between negative leak and temperature of calcium cathode in helium gas at 3.236 millims. pressure.

and combines with the platinum on the surface of the strip, to form an alloy from which the calcium only slowly vapourises away. After long heating the whole of the calcium could be driven off the platinum, and the negative leak was reduced to the value it had before the calcium was sublimed.

From the numbers given it will be seen that the leak from calcium is enormously greater than that from platinum at the same temperature. For example, at 1385° C. the leak from calcium is about 5000 times the leak from platinum, which means that there are 5000 times as many corpuscles liberated per second per square centimetre from calcium as from platinum at this temperature.

The values of the constant Q , deduced from successive pairs of these results, are given in the last column of Table IV.

The large variations in Q are most probably due to the experimental difficulties of measuring the negative leak from calcium. It was generally difficult to get a steady reading of the current at any temperature, for the leak increased and decreased in a capricious manner. Moreover, the series of observations had to be taken very quickly, because the leak gradually decreased with continual heating, owing to the calcium subliming away.

The mean value of the constant A , calculated from the temperatures and currents

per square centimetre, given in Table IV. is 1.71×10^4 , so that the equation for the current per square centimetre from calcium at θ° (absolute) becomes

$$x = 1.71 \times 10^4 \theta^{\frac{1}{2}} e^{-72,900/2\theta}.$$

The values of the negative leaks calculated from this formula are placed alongside the observed values in Table IV.

The agreement between the observed and calculated currents is not nearly so good as in the case of platinum. This is no doubt due to the difficulties attending the use of calcium. In the course of the experiments a note was made in the laboratory book that the currents recorded at 1050° C., 1065° C., and 1310° C. were steadily increasing during the observations. We see from the table above that the observed currents at these temperatures were considerably too low. If it had been practicable to have left the apparatus for a few minutes before measuring the leak, the values of the currents at these temperatures would, no doubt, have been nearer to the theoretical value. The experiments, however, show in a quite satisfactory manner that at a given temperature the rate of emission of negative corpuscles from calcium is much greater than in the case of platinum; and by applying the results to the formula employed we see that this increased rate of emission is due to a decrease in the value of the constant Q , that is, to a decrease in the energy required to set free the corpuscles from the surface of the platinum; for on any theory of the negative leak Q is a measure of the work required to produce a gramme molecular weight of corpuscles. The value found for Q for calcium (7.29×10^4) lies between the value found for platinum (1.219×10^5) and that obtained by RICHARDSON for sodium (6.32×10^4). This is what one would expect, and indicates that the amount of energy required to liberate the corpuscles is less the more electropositive the metal.

(4) *The Negative Leak from Lime.*

When the series of observations recorded in Table IV. had been made, the calcium on the platinum strip was oxidised to lime by letting into the apparatus some pure dry oxygen. The oxygen was prepared by the electrolysis of water and then passed over sticks of caustic potash and some fused calcium chloride. It was let into the apparatus to a pressure of 3 or 4 millims. On gradually raising the temperature of the cathode the negative leak was at first only slightly greater than before the oxygen was admitted, but soon it increased very rapidly as the calcium oxidised, and a pale glow appeared in the discharge tube. After this luminous discharge had once appeared the negative leak at all temperatures was much greater than before the oxygen had been admitted into the apparatus. The following table gives the negative leaks under a potential difference of 40 volts at various temperatures in helium, the excess of oxygen having been absorbed by sending a discharge for some

time through the tube containing the sodium-potassium alloy. The pressure of the helium was, as in the case of the calcium cathode, 3.236 millims.

TABLE V.

Temperature	Current in ampères per square centimetre.		Q (calories).
	Observed.	Calculated.	
° C.			
730	5.29×10^{-8}	3.73×10^{-8}	7.25×10^4
785	3.55×10^{-7}	4.57×10^{-8}	8.82×10^4
820	1.37×10^{-6}	1.98×10^{-6}	11.19×10^4
856	7.13×10^{-6}	8.14×10^{-6}	13.76×10^4
877	2.19×10^{-5}	1.79×10^{-5}	9.55×10^4
918	9.30×10^{-5}	7.61×10^{-5}	6.59×10^4
949	1.90×10^{-4}	2.14×10^{-4}	9.91×10^4
965	3.23×10^{-4}	3.57×10^{-4}	

Mean value of $Q = 9.58 \times 10^4$.

The observed currents in the above table are plotted against the corresponding temperatures in fig. 5. The curves obtained are of the usual form for the negative leak from glowing solids.

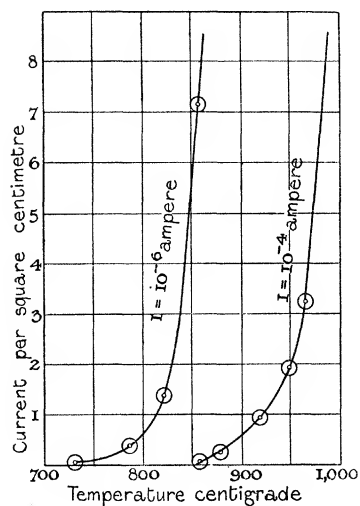


Fig. 5. Negative leak from lime in helium at a pressure of 3.236 millims.

By comparing Table V. with Table IV. it will be seen that the negative leak from lime is enormously greater than from metallic calcium under the same conditions, the leak from a lime cathode at 950° C. being about the same as the leak from calcium at 1400° C. This is contrary to what we should expect on the supposition that the negative leak is due to the escaping of the corpuscles from the cathode, for the presence of an atom of oxygen in the molecule of lime would hinder, by its attraction for negative electricity, the escape of the corpuscles, and we should expect, in consequence, that the negative leak from lime would be less, under the same conditions of temperature and pressure, than the negative leak from the same amount of calcium in the metallic state.

The values of the constant Q , deduced from successive pairs of observations, are given in the last column of Table V.

The variations in the value of Q are very considerable—nearly as large as in the case of the calcium cathode. Several other sets of observations of the negative leak from a lime-covered cathode were made, and in all cases there were considerable variations in the values of the constant Q , calculated from the experimental numbers. It should be mentioned that when the temperature was 877°C . a pale glow was observed in the gas on one side of the cathode. This extended to both sides of the cathode on raising the temperature to 918°C ., and became brighter at each subsequent increase of the temperature. The appearance of the glow was not marked by any abnormal increase in the current, as will be seen by the perfect continuity of the curve in fig. 5. The large values of Q obtained at this point seem to be purely accidental. From a large number of experiments with lime cathodes the mean value of Q , calculated from observations made just when the discharge became luminous, was not greater than the average value for the whole series of observations. The appearance of the luminous discharge will be treated of more fully in a later part of this paper.

The negative leak from the lime was tested again a few hours later. It was found to have decreased very considerably, and the luminous discharge did not now appear until the cathode had been raised to a much higher temperature than before. This was found to be a general rule, namely, that long continued heating of the lime diminished the negative leak. In the present case, after heating for about two hours to 1000°C ., the negative leak was only of about the same magnitude as in the case of the calcium cathode. This will be seen by comparing the numbers in the following table with those given for calcium in Table IV. :—

TABLE VI.—Negative leak from lime after heating to 1000°C . for two hours in helium gas at a pressure of 3.236 millimetres.

Temperature, °C.	Negative leak, ampères per square centimetre.	Temperature, °C.	Negative leak, ampères per square centimetre.
942	6.84×10^{-9}	1226	2.24×10^{-5}
1005	1.22×10^{-7}	1290	1.81×10^{-4}
1170	1.51×10^{-6}	1316	3.42×10^{-4}

The mean value of Q obtained from these observations is 1.34×10^5 —much greater than the mean value given in Table V. The luminous discharge was not observed in these experiments until the temperature was raised to 1316°C .

The mean value of the constant A calculated from the experimental numbers tabulated in Table V. is 6.42×10^{11} , so that the equation for the current per square centimetre from lime at the absolute temperature θ is

$$x = 6.42 \times 10^{11} \theta^{\frac{1}{2}} e^{-9.58 \times 10^4 / 2\theta}.$$

The currents calculated by means of this formula are given in the third column of Table V.

From these figures it will be seen that the formula only roughly represents the

observed results. The discrepancies may be due to the unsteadiness of the negative leak from lime which has been mentioned above. The leak was steadier than with the calcium cathode, but not nearly so steady as with the glowing platinum. The chief alteration of the leak was the gradual decrease as the heating of the cathode was continued. This may have been due to a diminution of the amount of lime by spluttering or by peeling off from the surface of the platinum, although no such phenomena could be observed. It is not due to a decomposition of the lime by electrolysis, for the author has shown* that no signs of electrolysis can be detected when a current is sent through a vacuum tube from a lime cathode, and further experiments with other lime cathodes showed that the negative leak decreased with continual heating of the cathode, whether the discharge was passed or not. The discrepancies between the observed and calculated values in Table V. follow from the discordant values found for the constant Q .

It has already been mentioned that a large series of experiments with lime cathodes all gave similar results. In order to see if these irregularities were peculiar to the present method of experimenting, the values of Q were calculated from WEHNELT's values of the negative leak from lime given in the 'Philosophical Magazine' for July, 1905, p. 87. The variations in the values of Q thus found were somewhat greater than those shown in Table V. The mean value was $Q = 50,900$ —considerably less than the value found in the present experiments. It thus seems that the negative leak from lime is subject to irregular variations, and does not obey the Wilson-Richardson law with anything like the accuracy of the leak from platinum.

The fact that the negative leak from calcium is greater than from platinum at the same temperature we have seen to be due to a decrease in the value of the constant Q , that is, to a diminution of the energy required for the liberation of the corpuscles. The value of Q for lime as found in the observations tabulated above is greater than the value for calcium, and the fact that the current is greater in the case of lime than in the case of calcium is due to the enormously greater value of the constant A in the former case.

A theory to account for the negative leak from hot metals has been proposed by RICHARDSON.† He supposes the negative leak to be due to the escape of the corpuscles which, on the ionic theory of metallic conduction, all conductors contain. The corpuscles are supposed to move about freely inside the conductor, and to have a distribution of velocities the same as the molecules of a gas. Corpuscles entering the surface layers of the conductor with a normal velocity component greater than a certain amount are supposed to escape into the surrounding space, and it is these corpuscles which maintain the current forming the negative leak. From these assumptions RICHARDSON has deduced a formula of the type $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, and has

* 'Phil. Mag.,' April, 1906, p. 506.

† O. W. RICHARDSON, 'Phil. Trans.,' A, vol. 201, p. 497.

shown that the constant A is proportional to the number of free corpuscles in a cubic centimetre of the conductor in question.

From experiments on the negative leak from hot platinum in air and in hydrogen H. A. WILSON* has come to the conclusion that the phenomenon cannot be completely explained by such a simple theory, and, moreover, he has shown that in order to obtain the above formula it is not necessary to make any assumption as to the manner of formation of the ions, but only to assume that they are produced in some way at the surface of the hot platinum. In WILSON's view, the constant Q is a measure of the work required to produce a gramme molecular weight of ions at the surface of the hot platinum, but experiments on the negative leak in hydrogen at different pressures have led to the conclusion that the constant A cannot be regarded as proportional to the number of corpuscles in a cubic centimetre of the cathode, and WILSON shows that the number so deduced does not agree with the value found by PATTERSON† from experiments on the variation of the resistance of platinum in a magnetic field. A comparison of the values of A found for lime and for calcium in the present research appears to support this view of WILSON's, for it does not seem possible that there can be 10^7 times as many free corpuscles in a cubic centimetre of lime as in a cubic centimetre of calcium. Further, it is well known that the electric conductivity of lime increases rapidly with rise of temperature. The author has shown that this conductivity is mainly, if not entirely, metallic in nature, and, on the ionic theory of metallic conduction, due to a large increase in the number of free corpuscles contained in the substance, for it is improbable that the velocity of the corpuscles increases to this extent. If, then, A is proportional to the number of corpuscles per cubic centimetre, its value should increase with the temperature. In the present experiments with lime, although there were considerable variations in the value of A calculated from the negative leaks at different temperatures, there was no sign of a progressive increase with increasing temperature.

From WEHNELT's work on the discharge of negative ions from glowing lime and other metallic oxides, RICHARDSON has drawn the conclusion that the corpuscles proceed not from the glowing oxide, but from the platinum, and that the oxide merely has the effect of lessening the amount of energy required to set them free. This conclusion is arrived at from the fact that the number of corpuscles per cubic centimetre calculated from the value of the constant A , as found from WEHNELT's numbers, is about the same as for platinum. The value of A for lime obtained in the present experiments is much greater than the value obtained for platinum, the former being 6.42×10^{11} and the latter 1.55×10^6 . Other experiments with lime-covered cathodes gave values ranging from $A = 1.23 \times 10^{10}$ to $A = 7.12 \times 10^{13}$, the value given by the observations recorded in Table VI., taken after the cathode had been heated for a long time to a high temperature. The values of A , calculated from observations

* H. A. WILSON, 'Phil. Trans.,' A, vol. 202, p. 243.

† PATTERSON, 'Phil. Mag.,' 6, III., 655.

with different cathodes, are thus seen to vary very considerably ; the values of Q , too, were not in very good agreement. It seems likely that this may be due to the platinum being more completely covered with lime in some cases than in others, for it will be readily understood that the cathode could not be quite uniformly covered with calcium at each attempt by the method of sublimation. In order to obtain more accurate knowledge of the values of these constants, experiments must be made with very carefully prepared lime cathodes. Meanwhile, the fact that a large emission of negative corpuscles takes place from a Nernst filament at high temperatures seems to indicate that in experiments with lime-covered cathodes the corpuscles proceed from the oxide, and not from the platinum underneath.

In view of the experiments of Professor WILSON, which have shown that the presence of hydrogen enormously increases the negative leak from platinum, it was thought to be interesting to see if the leak from lime was increased by admitting hydrogen into the apparatus. It was found that this is the case, the leak in hydrogen being many times greater than in helium or oxygen. The effect of introducing a little hydrogen into the apparatus is well shown by some observations taken with a lime cathode which had been used for some days, and the negative leak reduced to even a smaller amount than the values given in Table VI. The following are the values of the negative leak from such a cathode. The gas present was a mixture of helium and oxygen at a pressure of 3.91 millims. The voltage used was -40 volts.

TABLE VII.

Temperature, ° C.	1038	1382	1520
Negative leak in ampères	6×10^{-9}	1.32×10^{-5}	1.13×10^{-4}

The above numbers are the smallest values of the negative leak at the temperatures given that I ever obtained from a lime cathode. There was no sign of a luminous discharge, even at the highest temperature. After taking these observations, some pure dry hydrogen was let into the apparatus, and the cathode was gently warmed until no further diminution of pressure took place. The resulting gas was a mixture of helium and hydrogen at a pressure of 3.81 millims. A luminous discharge was now noticed when the temperature of the cathode was 1220° C. and the current passing 3.12×10^{-4} ampère. The glow in the gas was of a pale blue colour, and appeared only round the edges of the anodes. As the temperature of the cathode was gradually raised and the current passing increased, the glow became more extensive and brighter. At 1465° C. it was very white, and had gathered up into little balls about points on the rim of the anodes. Although the temperature was raised as high as was compatible with the safety of the cathode, and the current passing rose to one-twentieth of an ampère, no cathode glow was obtained. The following is a selection from a list of readings obtained in this series of experiments. The readings of the negative leak, at temperatures over 1250° C., were taken with a milliammeter. The

currents measured decreased rapidly as the heating of the cathode was continued, especially at the highest temperatures.

TABLE VIII.

Temperature, ° C.	Negative leak in ampères.	Temperature, ° C.	Negative leak in ampères.
895	9.85×10^{-8}	1380	4.5×10^{-3}
1013	5.69×10^{-6}	1465	1.4×10^{-2}
1220	3.12×10^{-4}	1535	2.7×10^{-2}
1293	1.2×10^{-3}	1620	4.7×10^{-2}

It is thus seen that the negative leak from lime is considerably increased by introducing hydrogen gas into the apparatus. H. A. WILSON has shown that hydrogen greatly increases the negative leak from platinum, and has come to the conclusion that the negative leak from platinum in air, or in a vacuum, is almost entirely due to traces of hydrogen in the metal. WILSON reduced the leak to $\frac{1}{250,000}$ part of that observed by RICHARDSON by taking precautions to remove such traces. It should be mentioned that the currents in the above table are much larger than the negative leaks from platinum in hydrogen obtained by WILSON, and the increase of current cannot be merely due to the effect of the hydrogen upon the platinum.

In another experiment a lime-covered cathode in oxygen at a low pressure (0.002 millim.) with a potential difference of 40 volts gave a negative leak of 4.6×10^{-4} ampère at 965° C. On pumping out the oxygen and letting hydrogen into the apparatus and then pumping down to the same pressure as before, the negative leak at temperatures below 900° C. was only slightly greater than the leak at the same temperature before the hydrogen was admitted, but at 980° C. a faint luminosity was seen in the gas round the cathode, and the negative leak increased *without the temperature of the cathode being raised or the difference of potential between the electrodes being altered*. This increase was slow for a few minutes, but afterwards became more rapid, and, although the temperature was lowered by putting more resistance in the heating circuit, the negative leak increased to 60 milli-ampères at 885° C. The luminous glow was then quite bright, and filled the whole bulb. It was at first thought that this sudden increase in the negative leak was due to the temperature of the cathode increasing while the discharge was passing, but experiments showed that the temperature of the cathode went up only a few degrees when the electric field was put on, and the leak gradually increased, even though the temperature, as indicated by the thermo-junction, was diminished by putting extra resistance in the heating circuit.

On allowing the cathode to cool down, and then again testing at lower temperatures, it was found that the negative leak at these lower temperatures was now much greater than at the first observations. A measurable leak was obtained at a much lower temperature than before, and the leak at 740° C. was 4.6×10^{-4} ampère—about 10^4 times as large as before the glow had been obtained in the discharge tube. On

gradually increasing the temperature the luminous discharge began without any sudden jump in negative leak taking place. I again found that after a certain temperature had been attained and a large current was passing, I could decrease the temperature of the cathode and still get the luminosity to continue and the current to pass.

These experiments show that the negative leak from lime is enormously increased by replacing the gas in the apparatus by hydrogen. With a lime cathode in hydrogen at a pressure of 0.01 millim. I obtained a current of 0.15 ampère per square centimetre at about 900° C., with a difference of potential of 40 volts between the electrodes. This is the largest negative leak I have measured under this potential difference.

The appearance of the luminous discharge is of great interest. Generally the luminosity began round the cathode, and was of a very faint blue colour, getting whiter and more extensive as the temperature of the cathode was increased. When the cathode was unequally covered with lime, the discharge could be seen to radiate out from a few points only. The appearance of the luminosity at any point depends on the current density at that point, and with a very evenly covered cathode large currents could be made to pass through the tube without any signs of a luminous discharge appearing. The appearance of the luminosity also depends on the potential difference between the electrodes. The luminosity could not be obtained with a potential difference of less than 18 volts; and it seems probable that this is the value of the anode fall of potential, for the cathode fall is reduced to a very small amount by the enormous emission of negatively charged corpuscles from the cathode.* As a rule, the luminous discharge gradually became visible, and increased in brightness as the temperature of the cathode was slowly raised. When the luminosity appeared gradually there was no sudden jump in the current passing. This is well illustrated in the curves of fig. 5. On the other hand, when the potential difference between the electrodes was much greater than 40 volts, the luminosity usually appeared quite suddenly and was accompanied by a sudden increase in the negative leak.

The current density obtained with a calcium-covered cathode was, generally, not sufficient to produce a luminous discharge, but on one occasion, on heating the cathode to a much higher temperature than usual, a faint luminosity was observed. This was at about 1520° C., and the current passing through the tube was 4 milli-ampères. Some interesting experiments were made with this cathode. The temperature was kept constant, and the potential difference between the electrodes was increased from zero by two volts at a time. No luminosity was obtained until a potential difference of 20 volts was reached. With this voltage a pale glow was seen round the *anode*. This glow increased in brightness as the voltage was increased. With 28 volts the glow left the anode and a pale luminosity appeared round the cathode. At the same time the current passing increased from being too small to

* WEHNELT, 'Phil. Mag.,' 6, vol. 10, 1905.

measure on a milliammeter to 2.8 milli-ampères. These experiments were performed in helium at a pressure of 3.28 millims. Similar results were obtained with lime cathodes. For instance, during the observations recorded in Table VIII. a faint luminosity was noticed round the edges of the anode when the cathode was at 1220° C. This luminosity increased in brightness as the temperature was raised, but with a potential difference of 40 volts the glow was always on the anode only. It was found that at 1410° C. it required a potential difference of 74 volts to give a luminosity round the cathode. With 72 volts there was a very bright anode glow, and the current passing was 4.5 milli-ampères. With 74 volts a brilliant cathode glow was obtained, and the current suddenly increased to 0.5 ampère. Further experiments showed that the difference of potential required to give the cathode glow was less the higher the temperature of the cathode.

The appearance of the luminosity round the cathode has been studied by Professor J. J. THOMSON,* who worked in a slightly different manner from that described above. By keeping the temperature of the cathode constant, and very gradually increasing the potential difference by means of a potential divider, Professor THOMSON found that the luminosity always appeared quite abruptly and was accompanied by a very rapid increase in the negative leak. In one case, at 1400° C., an increase in the potential difference of $\frac{1}{100}$ of a volt caused a bright luminosity to appear and increased the current forty-fold. A result similar to this was obtained in the experiments now recorded, when the cathode was at a high temperature and the voltage gradually increased; but if the temperature of the cathode was not too high, a luminosity round the anode was first obtained, and this at a certain potential difference appeared to leave the anodes and surrounded the cathode. This inversion of the appearance of the discharge was accompanied by a large increase in the current.

In the present experiments, when a difference of potential of 40 volts was used and the temperature of the cathode gradually increased, the luminosity appeared sometimes round the anodes and sometimes round the cathode, but always quite gradually, except when a cathode newly covered with lime was used. In this case the luminosity did not appear until a temperature higher than usual had been reached. Under these circumstances it generally appeared quite suddenly and then increased in brightness, although the temperature was kept constant or, in some cases, actually lowered.

Professor THOMSON has concluded from his experiments that the gas becomes luminous in consequence of the internal energy of the atoms increasing, under the bombardment of the corpuscles shot out by the cathode, to such an extent that the equilibrium of the atomic system becomes unstable and an explosion occurs. This explosion results in an expulsion of corpuscles and such a shaking up of those left in the atom that they vibrate so vigorously that the energy radiated is sufficient to produce luminosity. When the luminosity appears abruptly, we must imagine that

* Royal Institution Lecture, Friday, January 19, 1906.

just before it occurs the atoms are in such a state that a small change in the electrical conditions is sufficient to cause them to pass from a condition in which they are giving out no light to one in which they are brightly luminous. Now the current passing through the tube increases with the potential difference between the electrodes at a rate which increases rapidly with the temperature of the cathode. The higher the temperature of the cathode, therefore, the greater will be the effect of a given increase in the potential difference, and whereas at low temperatures the appearance of the luminosity may be quite gradual, the same increment in the potential difference may, at high temperatures, make all the difference between no glow and a very bright one, so that the luminosity appears quite suddenly. In the present experiments the gas pressure was so great that the current was never saturated, but increased at an ever increasing rate with the potential difference. Under these circumstances a similar argument will apply to the case of the potential being kept steady and the temperature being gradually increased. With a low potential difference between the electrodes the luminosity would be expected to appear gradually, and with a large potential difference to appear more abruptly. It has already been stated that this is what was observed.

The conditions which decide whether the luminosity appears round the anode or the cathode need further investigation and will form the subject of future research.

(5) *Summary of Results, and Conclusion.*

The results contained in this paper may be summarised as follows :—

1. The experiments with a platinum cathode show that the negative leak from platinum in helium or argon at low pressures is practically the same as in air or oxygen. The variation of the negative leak per square centimetre with the temperature can be expressed by an equation of the form used by H. A. WILSON and by O. W. RICHARDSON, viz., $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, where x is the current in ampères, θ the absolute temperature, and Q and A are constants. The values of these constants for a cathode well cleaned with nitric acid in helium at a pressure of 3.236 millims. with a potential difference of 40 volts between the electrodes are $Q = 1.22 \times 10^5$, $A = 1.55 \times 10^6$.

2. Attention has been drawn to a curious increase in the negative leak caused by allowing the cathode to stand for some time with a very low gas pressure in the apparatus. This increase seems to be caused by the appearance of a dark substance on the surface of the platinum cathode. The substance is probably produced by the action of the mercury vapour on the platinum. It could be driven away by long continued heating of the cathode.

3. The negative leak from calcium is enormously greater than from platinum at the same temperature. As with platinum, the variation of the leak with the temperature can be expressed by the equation $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/2\theta}$, but the observed values of the negative leaks from calcium at different temperatures do not so closely agree

with the values calculated from the equation as is the case with platinum. This is probably due to the greater experimental difficulties attending the use of calcium.

4. On oxidising the calcium on the cathode to lime there is an enormous increase in the negative leak, the leak from a lime cathode at 950°C . being about the same as the leak from calcium at 1400°C . The variation of the negative leak from lime with the temperature roughly obeys the Wilson-Richardson law, but the leak at any fixed temperature is not constant, but gradually decreases with continued heating. This diminution is not due to the same cause as the diminution of the leak from a new platinum wire. In the case of platinum the decrease is caused by the gradual evolution of gas—probably hydrogen—occluded in the metal. With lime it seems to be due either to a spluttering away of the lime from the surface of the platinum or to a change in the nature of the lime itself. In this connection it is interesting to note that a piece of lime subjected to a strong heat glows very brightly at first, but gradually loses this property of glowing when kept continuously at a high temperature. It is not improbable that there is some connection between these two phenomena. Experiments are at present being made with this idea in view.

5. The following are the values of the constants Q and A for platinum, calcium, and lime respectively, obtained from observations of the negative leaks under a potential difference of 40 volts in helium at a pressure of 3.236 millims. :—

Cathode.	Q (calories).	A .
Platinum	1.22×10^5	1.6×10^6
Calcium	7.29×10^4	1.7×10^4
Lime	9.58×10^4	6.4×10^{11}

The constant Q represents the work done by a gramme molecular weight of corpuscles in escaping from the surface of the cathode. We see from the numbers given above that this is least in the case of calcium, but owing to the great variations in the different values of Q obtained for lime and for calcium we cannot lay much stress on the difference between the mean values for these two cathodes given above. It would, of course, be expected that the corpuscles would escape more easily from the metal than from the oxide, for we should expect the presence of the electro-negative atom of oxygen in the molecule to act as an attracting force tending to retain the escaping corpuscle.

6. The greatly increased leak obtained by oxidising the calcium cathode into lime is due to an enormous increase in the value of the constant A . Reasons have been given for thinking that this constant cannot be proportional to the number of free corpuscles per cubic centimetre of the cathode as follows from RICHARDSON'S theory of the negative leak.

7. The negative leak from lime in hydrogen is much greater than that in air or helium.

8. When the current density through the discharge tube reaches a certain value (only obtained with a calcium or lime cathode) the gas becomes luminous. This

luminosity appears abruptly if the temperature of the cathode is high and the potential difference between the electrodes is gradually increased, or if a large potential difference is used and the temperature of the cathode is gradually raised. The abrupt appearance is accompanied by a large increase of the current passing through the tube. The luminosity cannot be obtained with a potential difference of less than 18 volts, which is probably the value of the anode fall of potential. With small differences of potential (between 18 and 40 volts) the luminosity appears quite gradually as the temperature of the cathode is raised, and without any sudden increase in the current passing.

With low potential differences the luminosity appears sometimes round the anode and sometimes round the cathode. In the former case it may be caused to leave the anode and to appear round the cathode by increasing the potential difference. This inversion of the appearance of the discharge is always accompanied by a large increase in the current.

In conclusion, I wish to say that my best thanks are due to Professor J. J. THOMSON for his advice and interest in these experiments, which were carried out at the Cavendish Laboratory.
